# Electrochemical Evaluation of $LaNi_{5-x}Ge_x$ Metal Hydride Alloys

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## ABSTRACT

We report a detailed evaluation of Ge-substituted $LaNi_5$ for electrochemical application as a negative electrode in alkaline rechargeable calls. Alloys with small substitutions of Ge for Ni show operating pressures, chargeability, cyclic lifetime, and kinetics for hydrogen absorption and desorption all superior to those found in many other substitute $LaNi_5$ alloys, These improved properties were achieved with a minimal reduction in hydrogen storage capacity.

## INTRODUCTION

One impediment to the widespread consumer use of $LaNi_5$ as a negative electrode in alkaline rechargeable batteries is its fast degradation of hydrogen absorption capacity experienced during charge-discharge cycling. An approach used to alleviate this degradation is to make substitutions of various metals for La as well as Ni. The partial substitution of solutes such as Ti,[1] Zr, Nd, and Ce[2] for La; and Co, Mn, Al, and Si[2] for Ni have been shown to be successful for improving the cyclic lifetime. Another benefit of ternary solute substitution is the decrease in plateau pressure of the metal hydride, making it feasible to operate a nickel-metal hydride (Ni-MH) cell at low internal pressures.

Sakai et al.[3] performed a rigorous evaluation of several metals, M, as ternary solutes in $LaNi_{5-x}M_x$. The equilibrium hydriding pressure of the alloy was found to decrease upon substitution in the order Ni > (Cr, Co, or Cu) > (Al or Mn), and the cyclic lifetime to increase in the order Mn < Ni < Cu < Cr < Al < Co. In all these ternary alloys, however, the improvements in the cyclic lifetime and plateau pressure are unfortunately accompanied by a decrease in the hydrogen absorption capacity, long activation, or slow kinetics. The use of Sn as a partial substituent for Ni in $LaNi_5$, on the other hand, was found to reduce the plateau pressure and hysteresis, while retaining most of the absorption capacity of the binary alloy." Furthermore, the Sn substituent was found to result in a 20-fold increase in the cyclic lifetime in gas-phase thermal cycling[5] and a cyclic lifetime comparable to a multi-component, mischmetal basal alloy in electrochemical charge discharge cycling.[6-8] The kinetics of electrochemical charge and discharge also became more facile upon Sn substitution. *

Encouraged by the improvement in the electrochemical performance of $LaNi_5$ upon Sn substitution, we began studies of alloys prepared with other substituents from the main group of the periodic table. Germanium is one of the promising ternary solutes thus identified. From gas-phase studies,[9,10] Ge substitution has been reported earlier to reduce the absorption pressures of $LaNi_5$. In this letter, we report the behavior of Ge-substituted $LaNi_5$ alloys as negative electrodes in alkaline electrolytes for Ni-MH cells. Solute compositions of x = 0.3 and 0.4 in $LaNi_{5-x}Ge_x$ were chosen for this study because these alloys are single phase and have plateau pressures below 1 atm,[9,11] and our present experimental test cells are more amenable to the study of alloys of low (≤1 atm) absorption pressure.

## EXPERIMENTAL

powder diffractometer using Co K$\alpha$ radiation ($\lambda$ = 1.7902Å). The gas-phase isotherms were obtained with an auto m ated Sievert's apparatus. The electrochemical measurements were performed on Teflon-bonded Ml] alloy disk electrodes (area = 0.09 $cm^2$), using an EG&G 2-/3 Potenti ostat/ Galvanostat and a 1?60 Solartron Frequency Response Analyzer integrated with an IBM - 1)(' The cycling of the prismatic electrodes (area = 6.45 $cm^2$) was performed in a negative- limited glass cell with NiOOH counter electrodes and an Hg/HgO reference electrode, using an Arbin Battery Cycler. The details on the experimental equipment anti sample ilrcpar-alien have been provided in our previous publication [8]

## RESULTS ANI]) DISCUSSION

Figure 1 shows the X-ray diffr action patterns of $LaNi_{4.7}Ge_{0.3}$, $LaNi_{4.6}Ge_{0.4}$, and the binary alloy, These diffraction patterns show that all materials arc of single (Haucke) phase. There is an increase in the unit ccl] volume upon the substituti on of Ge from a value of 86.8 Å$^3$ for $LaNi_5$, to 87.8 Å$^3$ for $LaNi_{4.7}Ge_{0.3}$ and 88.2 Å$^3$ for $LaNi_{4.6}Ge_{0.4}$, as may be expected from substitution of Ni with an element having a larger metallic radius. Figure 2 shows three pressure-com position-tem perature (p-c-']') isotherms comparing the Ge-substituted alloys to the binary alloy at 25°C. As may be seen from these isotherms, the equilibrium pressure of 2 atm for binary $LaNi_5$ decreases to below 1 atm upon Ge substitution at these compositions. This decrease in the equilibrium plateau pressure with increasing unit cell volume is consistent with the observations of Mendelsohn, et al.[12]

The gas-phase hydrogen absorption capacities of the (ic-substituted alloys are marginally lower than the binary alloy or the Sn-substituted alloys. The electrochemical capacities obtained with the Ge-substituted alloys are in the range of 250-300 mAh/g, and are comparable to that of Sn-substitute alloys or a multi-component, mischmetal based alloy Of composition $MmNi_{3.68}Co_{0.75}Mn_{0.4}Al_{0.3}$ (Fig. 3). The high measured electrochemical capacity of the $LaNi_{5-x}Ge_x$ alloys can be attributed in part to the reduced plateau pressure for hydrogen absorpt ion. The binary alloy, whit.i~ has a plateau pressure higher than 1 atm, is not charged effectively in our test cells, which maintain an internal pressure slightly above the ambient pressurc

The electrochemical kinetic parameters for the hydrogen absorption and desorption processes, measured by DC polarization (both linear and Tafel polarization) and AC impedance methods, are given in '1'able 1. "1'here is reasonable agreement among the values of the exchange current density (normalized by geometric area) obtained from these three methods. The ternary substitution of Ge in $LaNi_5$ resulted in an increase in the exchange current density, as observed earlier with Sn.[8] The improvement in the kinetics is almost comparable to a Sn-substituted alloy, $LaNi_{4.8}Sn_{0.2}$. In comparison to $LaNi_5$, the Ge-substituted alloys show improvement in all kinetic parameter-s except the Tafel slope on desorption In addition, the kinetic parameters for the (ic-substituted alloys are generally better than those of $LaNi_{4.8}Sn_{0.2}$. In $LaNi_{5-x}Sn_x$ alloys, the kinetics show a maximum at low compositions, x=0 1 or 0 2, but inc.leased Ge substitution seems to benefit the charge kinetics even at the higher compositions of the present study.

Finally, the electrochemical capacity of the Ge-substituted alloys during charge-discharge cycling in nc:,ative-limited, prismatic Ni-MH cells is shown in Fig. 4. The cells were charged over a 5 hour period at 4.5 mA/cm$^2$ (60 mA/g) to 11 So/O of charge return and discharged over a 2 hour period at 12.5 mA/cm$^2$ (1 50 mA/g) to -0.5 V vs. 11s/11s0. The cyclic lifetime of the Gc-substituted alloys is compared with $LaNi_{4.75}Sn_{0.25}$ and a misch-metal based alloy evaluated earlier. The Ge-modified alloys have initial capacities slightly 1o wer that those of the best Sn-substitued alloys, but similar to those with the same Ni composition, Furthermore, some Gc-modified alloys experience a quick loss of some capacity in the first 30 cycles, This initial decline is not a function of the activation cycles and is being investigated. Despite this initial drop in capacity, the capacity retention of the Ge-modified alloys is excellent, especially in the latter stages of cycling. The rate of reduction in capacity after the initial fall is considerably less with the Ge-substituted alloys than in the Sn-substituted and misch-metal based Ml 1 alloys. Rates of capacity fade were 0.65 and 0.28 mAh/g/cycle for $LaNi_{4.7}Ge_{0.3}$ and $LaNi_{4.6}Ge_{0.4}$, 0.73 for $LaNi_{4.75}Sn_{0.25}$, and 0.72 for the misch metal based MH alloys. The capacity of the $LaNi_{4.6}Ge_{0.4}$ alloy after the first 100 cycles exceeds that of any of the Sn-substituted alloys as well as the misch-metal based formulations.

## CONCLUSIONS

The substitution of 6% and 8% of Ni with Ge in $LaNi_5$ improves its performance as an anode in alkaline rechargeable cells. The reduced absorption pressures facilitate the charging process and thus enhances the electrochemical capacity. Germanium substitution also leads to better absorption/desorption kinetics. More significantly, Ge substitution endows the material with excellent capacity retention during charge-discharge cycling. Overall, the effects of Ge substitution are similar to those of Sn, although the cyclic lifetime is superior. Detailed studies with the other Ge-based formulations are underway.

## ACKNOWLEDGEMENTS

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## FIGURE CAPTIONS

Fig 1: X-ray diffraction patterns of $LaNi_{4.6}Ge_{0.4}$, $LaNi_{4.7}Ge_{0.3}$, and $LaNi_5$. Powders were activated with 4 gas-phase hydrogen absorption-desorption cycles before measurement

Fig. 2: Gas-phase p-c-T isotherms of (-) $LaNi_5$, (■) $LaNi_{4.7}Ge_{0.3}$, and (●) $LaNi_{4.6}Ge_{0.4}$ measured at 23°C

Fig. 3: Capacities of (●) $LaNi_{5-x}Ge_x$ and (■) $LaNi_{5-x}Sn_x$ measured by (open symbols) gas-phase absolution to 5 atm. and (closed symbols) prismatic cells. Horizontal line rep{-cscnls capacity of $MmNi_{3.68}Co_{0.75}Mn_{0.4}Al_{0.3}$ measured in prismatic cell.

Fig. 4: Cyclic lifetimes of negative limited Ni-MH cells. 1) (···) $LaNi_{4.7}Ge_{0.3}$, 2) (-·-) $LaNi_{4.6}Ge_{0.4}$, 3) (---) $LaNi_{4.75}Sn_{0.25}$, and 4) (- ) $Mm(NiCoMnAl)_5$

Table I : Kinetic Parameters of $LaNi_{5-x}M_x$ Alloys in 5.S M KOH solution.

| Alloy | Micro-polarization i. [mA/cm²] | Tafel Polarization [mA/cm²] | Slope [mV/decade] Abs. | Des. | AC Impedance $i_0$ [mA/cm²] |
|---|---|---|---|---|---|
| $LaNi_5$ | 8.6 | 10.7 | 242 | 10s | **11.3** |
| $LaNi_{4.8}Sn_{0.}$ | 11.3 | **32,7** | 185 | 220 | 12.8 |
| $LaNi_{4.7}Ge_{0.}$ | 12.0 | 38.3 | 195 | 182 | 12.9 |
| $LaNi_{4.6}Ge_0$ | 12.7 | 31.7 | 217 | 84 | 13.4 |

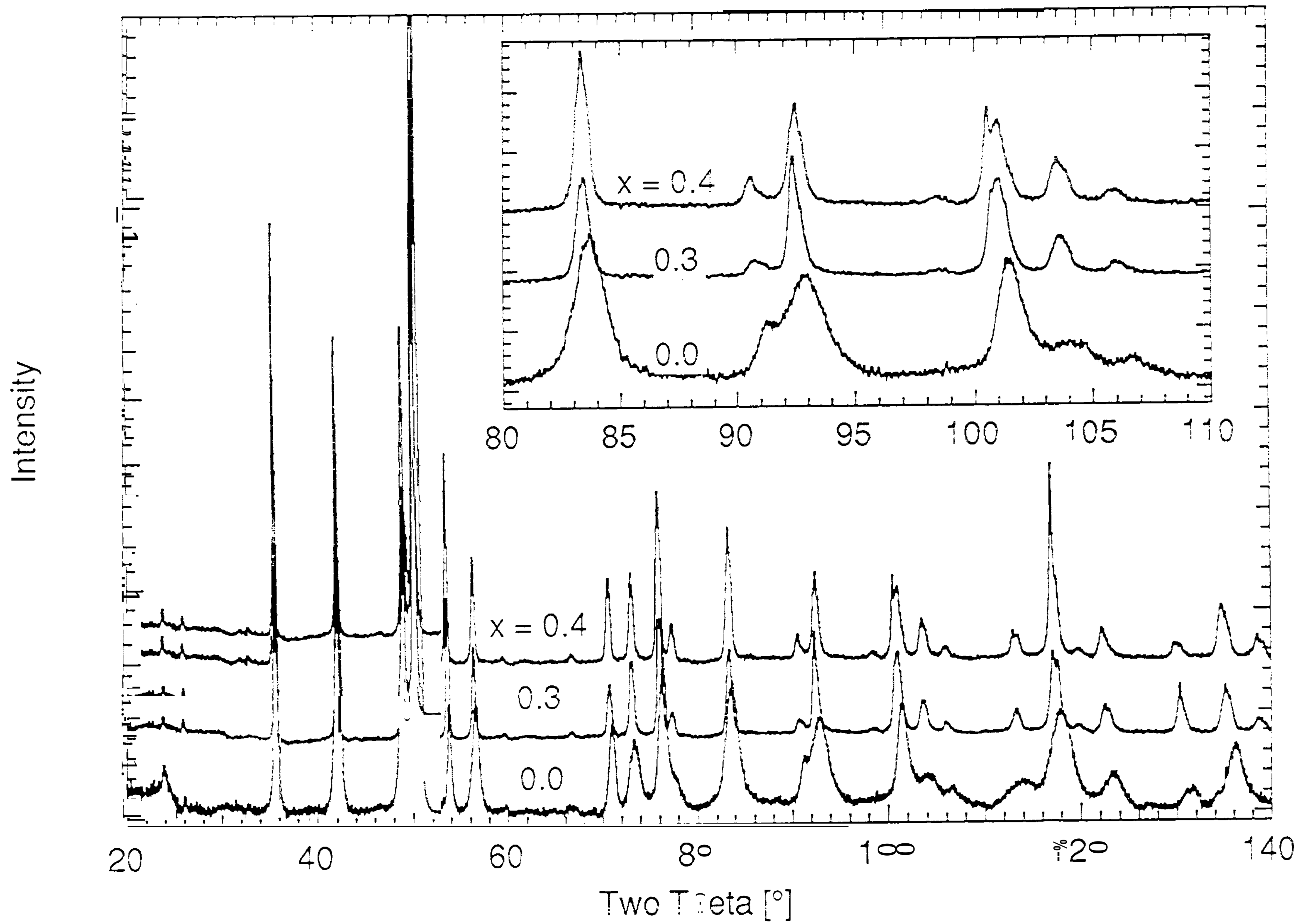


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Figure

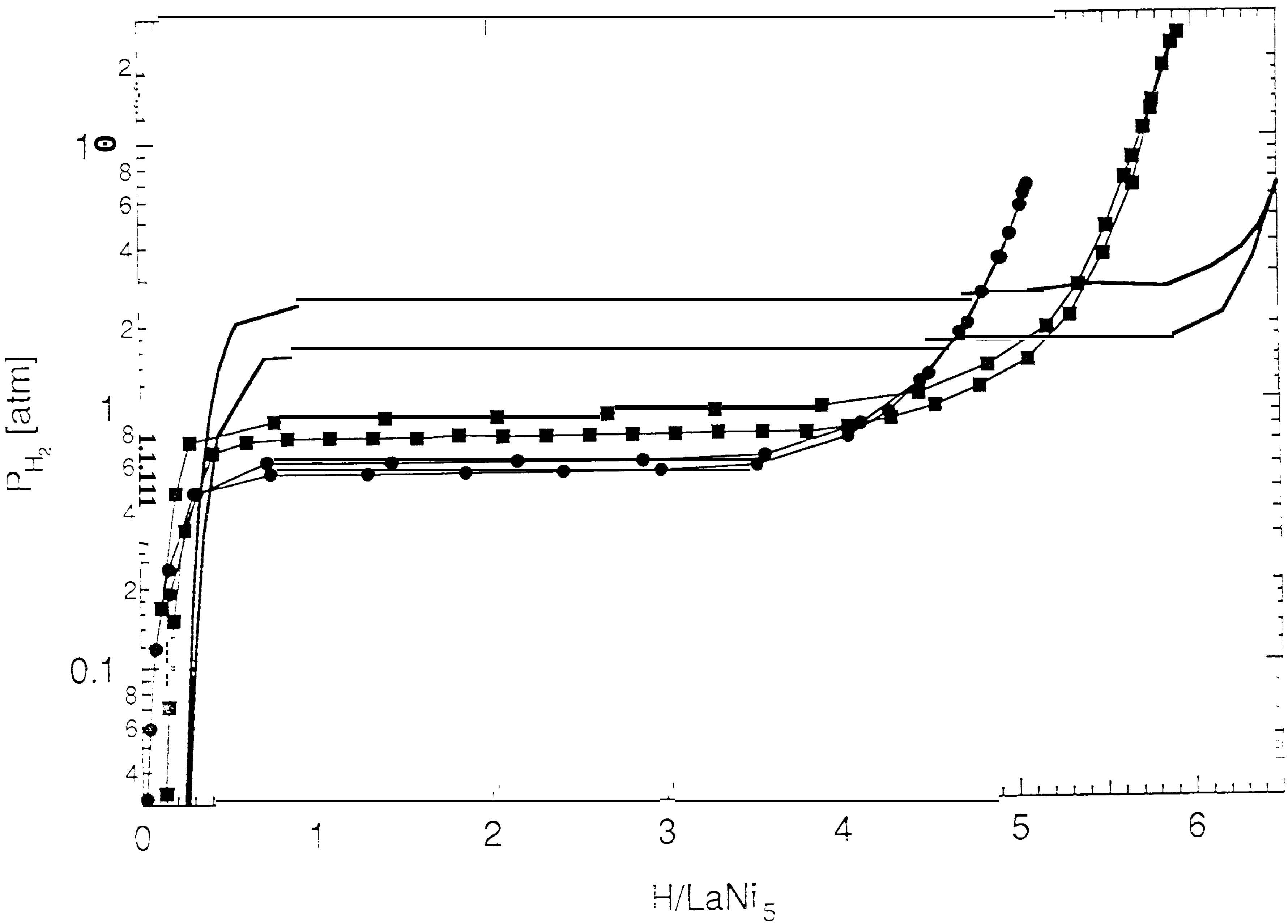


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Figure 2

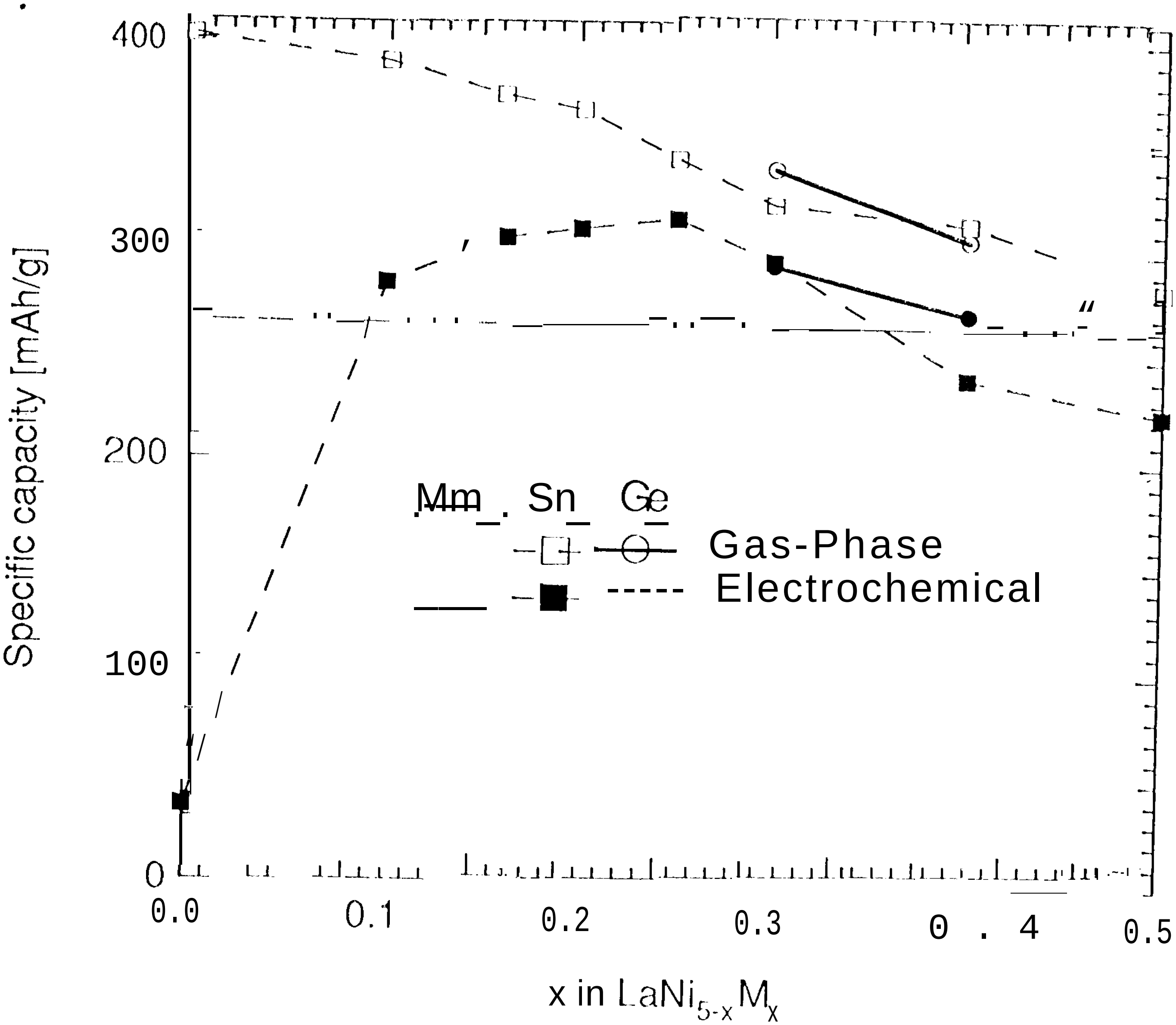


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Figure 3

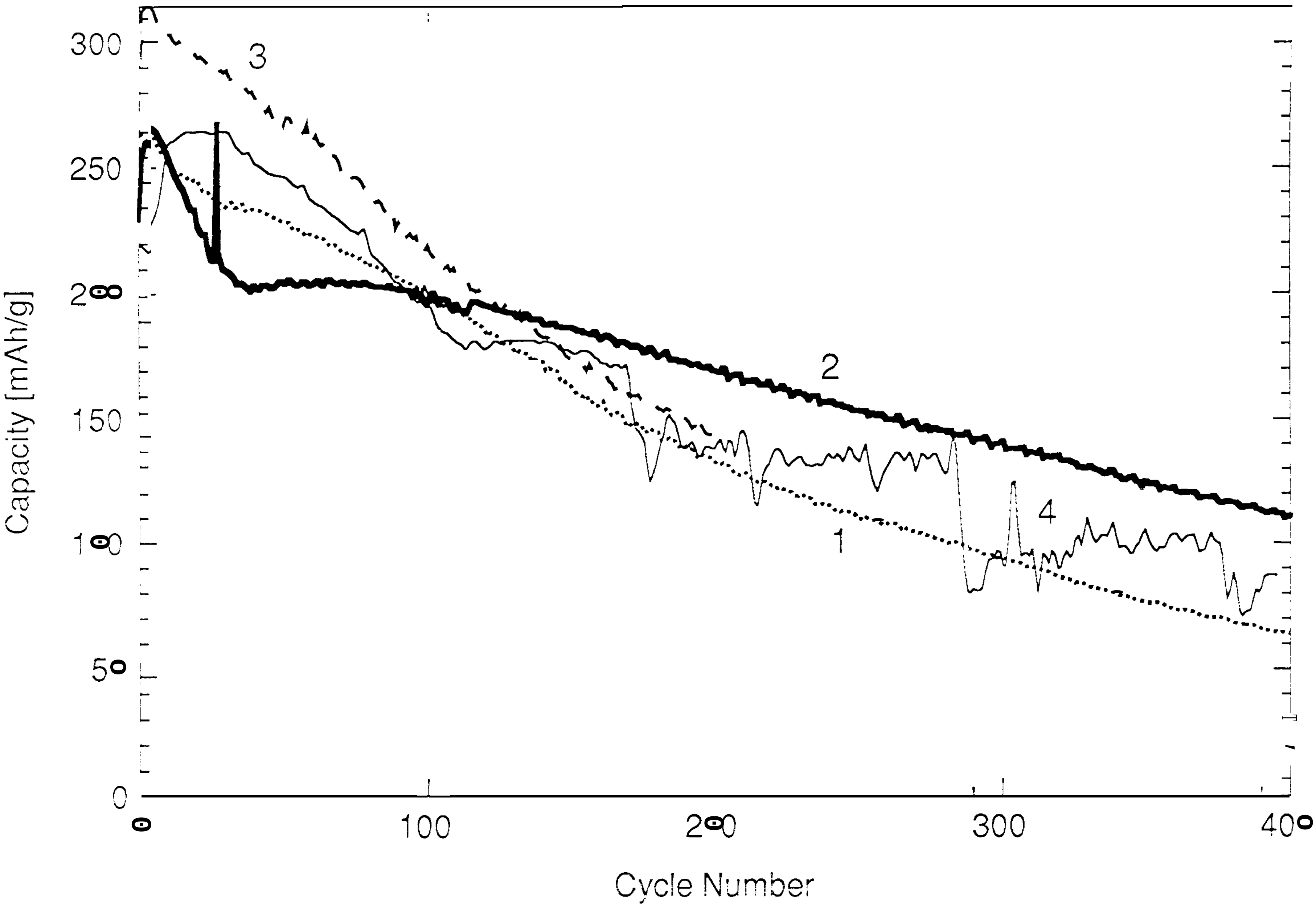


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Figure 4